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COMMITTEE OF EXPERTS ON THE
TRANSPORT OF DANGEROUS GOODS

Sub-Committee of Experts on the
Transport of Dangerous Goods
(Fifteenth session,
Geneva, 29 June-10 July 1998,
agenda item 5 (g))

MISCELLANEOUS DRAFT AMENDMENTS TO THE MODEL REGULATIONS ON THE TRANSPORT OF DANGEROUS GOODS

Toxic by inhalation substances
Definition and list

Transmitted by the Expert from the United States of America

Introduction

1. The Sub-Committee at its fourteenth session considered the definition of "toxic by inhalation substances" (TIH substances) on the basis of ST/SG/AC.10/C.3/1997/81. While agreeing that additional provisions on hazard communication should be provided for TIH substances, the Sub-Committee did not conclude its discussion on how this group of substances should be defined (see paragraph 119 of ST/SG/AC.10/C.3/28). The purpose of this paper is to elaborate on the proposed definition in ST/SG/AC.10/C.3/1997/81. In addition, document ST/SG/AC.10/C.3/1997/81 also identified substances meeting the proposed definition. Revised lists of substances are carried forward in this paper and potential issues with respect to the lists are discussed.

2. It is important to note that while it is necessary to come to a common understanding of a definition of "toxic by inhalation substances", it is not necessary to include a definition in the Model Regulations. Rather, the term will instead be used in applying requirements to individual substances. Therefore, in considering what substances should be captured by the term "toxic by inhalation substances" it is important to consider what substances warrant special packaging and hazard communication requirements.

Proposed definition of TIH substances

3. In document ST/SG/AC.10/C.3/1997/81, the expert from the United States had proposed that the TIH substances be limited to substances of Division 2.3 (where the only potential implication would be a change in labelling) and Division 6.1 substances that meet the vapour inhalation toxicity criteria for Packing Group I.

4. Based on discussions at the fourteenth session, the expert from the United States considers the following to be contentious issues with respect to the definition of TIH substances:

1. Whether gases meeting the criteria of Division 2.3 should be included; and
2. Whether the criteria for Division 6.1 TIH substances should be expanded or contracted.

5. **Division 2.3**. With respect to including Division 2.3 substances, it should be noted that the only implication of TIH proposals identified in papers submitted would be to amend the label used to identify Division 2.3 substances to coincide with the label proposed for Division 6.1 TIH substances. On this basis, it is proposed that the issue of whether to include Division 2.3 substances should be delayed until a decision is made on whether to provide a separate label for TIH substances.

6. **Defining TIH substances to encompass a smaller group of substances in Division 6.1**. A review of special packaging requirements applicable to Division 6.1 substances in other regulations (US, IMO, ADR/RID) on the basis of inhalation toxicity seems to confirm that the range proposed is appropriate.

7. **Defining TIH substances to encompass a larger group of substances in Division 6.1**. The UN Model Regulations includes both vapour inhalation criteria and dust and mist inhalation toxicity criteria for liquids and solids in Chapter 2.6. Clearly any substance that meets the inhalation criteria in Chapter 2.6 could be described as a substance that is toxic by inhalation. One possible definition would be to include all of these substances. The expert from the United States believes that this would be inappropriate for the following reasons:

1. The additional substances owing to their lower level of danger do not warrant special packaging and hazard communication requirements. In particular, substances meeting only the inhalation by dust and mist criteria should be excluded as transport incidents seldom involve conditions resulting in sustained evolution of dusts and mists. Substances meeting the packing group II and III vapor inhalation criteria should also be excluded owing to the lower risk that they pose due to their lower volatility and lower toxicity.

2. The intention of the hazard communication proposals is to call special attention to substances that have a particularly high degree of danger. Expanding the definition of TIH substances would substantially increase the list of substances and have the effect of reducing the significance of the message being conveyed by the hazard communication requirements.

8. In summary, the expert from the United States proposes that for the purpose of defining the group of TIH substances for which additional packaging and hazard communication requirements should be applied should be defined as:

gases which meet the criteria of Division 2.3, and

liquids that meet the vapour inhalation toxicity criteria of Division 6.1 at Packing Group I.

Subdivision of Division 6.1 Packing Group I substances

9. For purposes of assigning packaging requirements, it is also proposed that TIH substances of Division 6.1 be subdivided into two groups according to their degree of toxicity. Under the harmonization of classification criteria agenda item, the Committee has supported the OECD proposal to provide an inhalation toxicity breakpoint of 250 ml/m^3. It is proposed that this breakpoint be used to subdivide Division 6.1 substances and that, consistent with the approach already taken in the Model Regulations, a minimum vapor pressure be associated with this breakpoint. It is proposed that Packing Group I be subdivided into two groups as follows:

Group IA - substances with an inhalation toxicity of 250 ml/m^3 or less and $V \geq 500LC_{50}$; and

Group IB - substances with an inhalation toxicity of less than or equal to 1000 ml/m^3 and $V \geq 10LC_{50}$.

It should be noted that in the proposals on TIH substances this distinction will not be used in proposed hazard communication requirements.

Lists of liquids meeting the proposed TIH substances definition.

10. In document ST/SG/AC.10/C.3/1997/81 substances considered to meet the Division 6.1 packing group I inhalation toxicity criteria are identified. Due to a lack of time, the Sub-Committee did not discuss issues arising out of this substances list.

11. The lists of substances considered by the expert from the United States to meet the criteria of Division 6.1 packing group I inhalation toxicity criteria along with relevant data are shown in the Annex hereto. The substances have been subdivided into two groups which are provided in two separate lists according to the grouping criteria proposed above.

Potential issues

12. In providing the lists, it should be clear that **the lists are not being provided with the intention of reclassifying substances**. In addition to substances that are classified as Division 6.1 substances, the lists in Annex 1 also include substances classified as Division 5.1 and Class 8 substances. It is not intended that these substances be reclassified as substances of Division 6.1 on the basis of this paper. The purpose of this paper is solely to identify substances to which additional packaging and hazard communication requirements should be applied. Reclassification would have to be done on the basis of a complete data sheet.

13. **It is proposed that the additional requirements be applied to some substances even though the available data is incomplete.** While LC_{50} or vapor pressure data is available for the majority of substances, there are some substances where the LC_{50} or vapor pressure is unknown. These substances may be listed either on the basis of an LC_{lo} value obtained from the literature or on the basis of estimates based on a known LC_{50} for a similar substance. The United States has regulated substances as TIH substances for a number of years on the basis of these lists. Where industry disagreed with estimates, toxicological data has been provided and the lists were revised accordingly. In the case of a substance for which no LC_{50} data has been provided it can only be assumed that the estimates are valid or that there is no longer a commercial interest in transporting the substance. In the case of TIH substances, it is appropriate to err on the side of safety. It is, therefore, recommended that the assignment of packaging and hazard communication be done on the basis of the lists in the Annex hereto even when the actual LC_{50} or vapor pressure is unknown.

Annex

List of substances in the United Nations' Dangerous Goods List
known to be toxic by inhalation

LIST OF GROUP IA SUBSTANCES							
UN NO.	***SUBSTANCE***	***LC50 (ppm)***	***LCLo (ppm)***	***NOTE***	***V (20° C) (ppm)***	***NOTE***	***RTECS*****
UN 2484	tert-Butyl isocyanate	22	--	A	19700		NQ8300
UN 1745	Bromine pentafluoride	--	50	eS	453000		EF9350
UN 1744	Bromine	113	--	R*m	237000		EF9100
UN 1092	Acrolein, inhibited	25	--	D	289000		AS1050
UN 1834	Sulfuryl chloride	131	--	C	142000		WT4870
UN 2482	n-Propyl isocyanate	44	--	A	69700		NR0190
UN 1380	Pentaborane	12	--	R*	225000		RY8925
UN 1259	Nickel carbonyl	18	--	R*	422000		QR6300
UN 1251	Methyl vinyl ketone, stabilized	5	--	C*	93400		EM9800
UN 2480	Methyl isocyanate	22	--	A*	458000		NQ9450
UN 1244	Methylhydrazine	68	--	R*	50300		MV5600
UN 1185	Ethyleneimine, inhibited	76	--	R*	217000		KX5075
UN 2481	Ethyl isocyanate	--	--	14	--		NQ8825
UN 1239	Methyl chloromethyl ether	160	--	R*	210000		KN6650
UN 1238	Methyl chloroformate	88	--	R	135000		FG3675
UN 2605	Methoxymethyl isocyanate	--	--	14	--		NQ9240
UN 1051	Hydrogen cyanide, stabilized	40	--	R*	842000		MW6825
UN 2483	Isopropyl isocyanate	--	--	14	--		NQ9230
UN 2486	Isobutyl isocyanate	--	--	14	--		NQ9208
UN 1994	Iron pentacarbonyl	6	--	R?	30300		NO4900

LIST OF GROUP IB SUBSTANCES							
UN NO.	*SUBSTANCE*	*LC50 (ppm)*	*LCLo (ppm)*	*NOTE*	*V (20°C) (ppm)*	*NOTE*	*RTECS***
UN 2488	Cyclohexyl isocyanate	15	--	A	2170		NQ8650
UN 2407	Isopropyl chloroformate	299	--	A	36800		LQ6475
UN 2521	Diketene, inhibited	551	--	A	10500		RQ8225
UN 1143	Crotonaldehyde, stabilized	93	--	R*	42100		GP9499
UN 3079	Methacrylonitrile, inhibited	656	--	R*	84200		UD1400
UN 3246	Methanesulfonyl chloride	205	--	A	2760		--
UN 2382	Dimethylhydrazine, symmetrical	680	--	C*	92000	25°C	MV2625
UN 1647	Methyl bromide and Ethylene dibromide mixtures, liquid	--	--	14	--		PA5300
UN 1613	Hydrocyanic acid, aqueous solutions	--	--	14	--		MW6840
UN 2646	Hexachlorocyclopentadiene	3	--	R*	100		GY1225
UN 1605	Ethylene dibromide	650	--	A	11300		KH9275
UN 2644	Methyl iodide	448	--	R*	414000		PA9450
UN 1135	Ethylene chlorohydrin	74	--	A	6450		KK0875
UN 2477	Methyl isothiocyanate	635	--	C	27400		PA9625
UN 2606	Methyl orthosilicate	200	--	C	13300		VV9800
UN 1892	Ethyldichloroarsine	36	--	R*	2800		CH3500
UN 2826	Ethyl chlorothioformate	138	--	C	10900		LQ6950
UN 2032	Nitric acid, red fuming (NO2)	134	--	R*	55300		QU5900
UN 1754	Chlorosulfonic acid	16	--	C	1320	25°C	FX5730

LIST OF GROUP IB SUBSTANCES							
UN NO.	*SUBSTANCE*	*LC50 (ppm)*	*LCLo (ppm)*	*NOTE*	*V (20° C) (ppm)*	*NOTE*	*RTECS***
UN 1580	Chloropicrin	--	50	R*h	26100		PB6300
UN 3023	tert-Octyl mercaptan	102	--	R*	5000		MJ1500
UN 2232	2-Chloroethanal (Chloroacetaldehyde)	160	--	A	24300		AB2450
UN 1752	Chloroacetyl chloride	660	--	C	24600		AO6475
UN 2668	Chloroacetonitrile	--	500	R*	13200		AL8225
UN 1182	Ethyl chloroformate	145	--	R	55300		LQ6125
UN 1670	Perchloromethyl mercaptan	--	69	R*	32900		PB0370
UN 1672	Phenylcarbylamine chloride	--	1	20000		e	NJ6700
UN 2487	Phenyl isocyanate	16	--	A	2470		DA3675
UN 2337	Phenyl mercaptan	66	--	R*	1450		DC0525
UN 1810	Phosphorus oxychloride	96	--	R*	35500		TH4897
UN 1809	Phosphorus trichloride	208	--	R*	125000		TH3675
UN 1695	Chloroacetone, stabilized	262	--	R	41900		UC0700
UN 2485	n-Butyl isocyanate	105	--	C	13900		NQ8250
UN 2743	n-Butyl chloroformate	--	--	1	9870		LQ5890
UN 1569	Bromoacetone	--	95	R*h	11900		UC0525
UN 1746	Bromine trifluoride	50	--	eS	9200		EF9360
UN 2740	n-Propyl chloroformate	319	--	Rm	25500		LQ6830
UN 1595	Dimethyl sulfate	17	--	R*	1000		WS8225

LIST OF GROUP IB SUBSTANCES							
UN NO.	*SUBSTANCE*	*LC50 (ppm)*	*LCLo (ppm)*	*NOTE*	*V (20°C) (ppm)*	*NOTE*	*RTECS***
UN 1828	Sulfur chloride (mono)	327	--	C	8950		WS4300
UN 1829	Sulfur trioxide, inhibited	347	--	C	98700		WT4830
	Sulfur trioxide, stabilized						
UN 1831	Sulfuric acid, fuming (=,>30% free SO3)	347	--	R	=,>3470		WS5605
UN 1163	Dimethylhydrazine, unsymmetrical	504	--	R*	206000	25°C	MV2450
UN 1510	Tetranitromethane	36	--	R*	11000		PB4025
UN 2474	Thiophosgene	--	--	1	150000		XN2450
UN 1838	Titanium tetrachloride	119	--	R*	12800		XR1925
UN 2692	Boron tribromide	--	--	1	73700		ED7400
UN 1560	Arsenic trichloride	--	56	R*m	11500		CG1750
UN 1722	Allyl chloroformate	61	--	C	20400		LQ5775
UN 2334	Allylamine	590	--	R*	261000		BA5425
UN 1098	Allyl alcohol	253	--	R*	26000		BA5075
UN 1541	Acetone cyanohydrin, stabilized	--	126	R*	13200		OD9275
UN 2438	Trimethylacetyl chloride	507	--	C	35500		AO7200
UN 2442	Trichloroacetyl chloride	128	--	R*	22700		A07140

KEY (FOR BOTH LISTS)

**	RTECS numbers are given here without the three additional zeros that appear in the nin-position sequence number
1	These materials are considered to be toxic by inhalation although no inhalation data are available.
14	These materials are considered to be toxic by inhalation although no inhalation data or V data are available.
A	Data obtained from requests for approvals by the U.S. competent authority.
C	Data obtained through private consultation.
R	Data obtained from the RTECS.
e	Estimated.
h	Test involved humans.
m	Test involved mice.
*	LC50 value converted to 1 hour.
GROUP	See paragraph 9 of the main document.
RTECS	Registry of Toxic Effects of Chemical Substances (NIOSH).

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Geneva, 29 June-10 July 1997,
agenda item 5(a))

MISCELLANEOUS DRAFT AMENDMENTS TO THE MODEL REGULATIONS ON THE TRANSPORT OF DANGEROUS GOODS

Listing and classification

Special provision for mixtures of gases with oxidizing potentials greater than air

Transmitted by the Expert from the United States of America

Background

1. Two gas mixtures contained in the Dangerous Goods List are mixtures of oxygen and a non-oxidizing gas, (i.e. UN 1014, UN 1980). These mixtures are currently not identified as having a Division 5.1 subsidiary risk. However, as the oxygen concentrations for these entries are not specified, mixtures transported under these entries may or may not meet the oxidizing gas criteria as specified in 2.2.2.1(b)(ii).

2. It is proposed that a special provision be applied to each of these entries to the effect that a Division 5.1 label shall be applied if the gas mixture meets the criteria of Division 5.1.

3. In this respect, it is noted that in the case of some commercial gas mixtures containing oxygen, the oxygen concentration is frequently limited to a concentration of 23.5%. For example, the oxygen concentration of artificial air typically ranges from 19.5% to 23.5%. These values have been used in practice for many years. For practical reasons it is proposed that the special provision establish a limit of 23.5% as the concentration limit for when these gas mixtures are required to bear an oxidizing label.

Proposal

4. Create a new special provision XXX (below) and apply it to UN 1014 and UN 1980.

XXX Gas mixtures containing more than 23.5% oxygen shall bear the Division 5.1 oxidizing substance label.